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European Patent Office  
Office européen des brevets

(11) Publication number:

0 158 229  
A1

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 85103690.5

(51) Int. Cl.4: C 08 G 65/10

(22) Date of filing: 27.03.85

C 08 G 65/20, C 08 G 18/48

(30) Priority: 28.03.84 JP 58485/84  
16.11.84 JP 240481/84  
21.11.84 JP 244340/84  
21.11.84 JP 244345/84  
08.03.85 JP 44679/85

(72) Inventor: Aoshima, Atsushi  
42-5, Sumiregaoka Kohoku-ku  
Yokohama-shi Kanagawa-ken(JP)

(43) Date of publication of application:  
16.10.85 Bulletin 85/42

(72) Inventor: Tonomura, Shoichiro  
A-25, Endo-Apartment 68, Aoshimacho  
Fuji-shi Shizuoka-ken(JP)

(84) Designated Contracting States:  
DE FR GB NL

(72) Inventor: Fukui, Hiroyuki  
Asahi Kasei-Seiwa-Ryo 351-1, Samejima  
Fuji-shi Shizuoka-ken(JP)

(71) Applicant: Asahi Kasei Kogyo Kabushiki Kaisha  
2-6, Dojimahama 1-chome Kita-ku  
Osaka-shi Osaka 530(JP)

(72) Inventor: Imai, Hisaya  
A-34, Endo-Apartment 68, Aoshimacho  
Fuji-shi Shizuoka-ken(JP)

(74) Representative: Strehl, Schübel-Hopf, Schulz  
Widenmayerstrasse 17 Postfach 22 03 45  
D-8000 München 22(DE)

(54) Process for producing polyether polyol, the produced polyether polyol and polyurethane.

(57) A process for producing a polyether polyol with a content of 0.5 to 99.5 % by weight of oxytetramethylene groups derived from tetrahydrofuran by copolymerizing tetrahydrofuran or a mixture of tetrahydrofuran and other cyclic ether copolymerizable therewith with a polyhydric alcohol having two or more hydroxyl groups per one molecule with the use of a heteropoly-acid and/or its salt as a catalyst, which comprises allowing 0.1 to 15 molecules of water per one heteropoly-anion to exist in the catalyst phase.

The above-described polyether polyol is an industrially useful polymer which is a starting material for polyurethane to be used for spandex or a synthetic leather, etc.

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DESCRIPTION

TECHNICAL FIELD

The present invention relates to a process for  
5 producing a polyether polyol, which comprises copoly-  
merizing a polyhydric alcohol having two or more  
hydroxyl group in one molecule with tetrahydrofuran  
(hereinafter sometimes abbreviated as "THF"), or a poly-  
hydric alcohol with tetrahydrofuran and a cyclic ether  
10 copolymerizable therewith by using a heteropoly acid  
and/or its salt as a catalyst, and also to a novel  
polyether polyol.

BACKGROUND ART

For a polyether glycol, which is a starting  
15 material for a polyurethane to be used for spandex or a  
synthetic leather, polyoxytetramethylene glycol (here-  
inafter abbreviated as "PTMG"), which is a homopolymer  
of THF, has primarily been used. However, the soft  
segments of the urethane elastomer employing PTMG are  
20 liable to be crystallized at lower temperatures to cause  
problems in physical properties at lower temperatures  
such that recovery after being elongated under stress is  
not sufficients.

As one method for solving this problem, in-  
25 vestigations have been made about copolymers of THF with  
cyclic ethers as a substitute of polyether glycols for  
PTMG. However, due to difficulty in ring opening poly-  
merizability of a cyclic ether or in a synthesis of a  
cyclic ether, only limited species of copolymers are  
30 available and therefore no satisfactory result has yet  
been obtained.

In addition, generally ring-opening polymerizability of THF is low, and it has not yet been known to obtain a copolymer having both terminal ends of hydroxyl groups all at once by copolymerizing THF with a polyhydric alcohol co-presented therewith. It has only been known that epichlorohydrin, which is high in ring-opening characteristic, is allowed to co-exist with THF (see Japanese Patent Publication after examination No. 32200/1973). However, the polyhydric alcohols added in this method may be considered to act only for an initiation of the reaction, and therefore they are bonded only to one terminal end of the polymer.

The present inventors have made extensive studies to overcome those problems as described above and consequently discovered a catalyst which is capable of synthesizing a polyether glycol by copolymerizing a diol with THF to accomplish the present invention.

#### BRIEF DESCRIPTION OF DRAWING

Fig. 1 shows  $^1\text{H-NMR}$  spectrum of a copolymerized polyether glycol of THF and ethylene glycol as described in Example 1 (measured at 400 MHz by means of JEOL JNM-GX 400 NMR device);

Fig. 2 shows  $^{13}\text{C-NMR}$  spectrum of a copolymerized polyether glycol of THF and ethylene glycol, of which terminal hydroxyl groups have been acetylated, as described in Example 1 (measured by means of JEOL JNM-GX 400 NMR device);

Fig. 3 shows a schematic flow chart of a continuous polymerization device which can be used in practicing the process of the present invention;

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Fig. 4 shows  $^1\text{H-NMR}$  spectrum of a copolymerized polyether glycol of THF and 1,6-hexane diol as described in Example 2 (measured at 400 MHz by means of JEOL JNM-GX 400 NMR device);

5 Fig. 5 shows  $^1\text{H-NMR}$  spectrum of a copolymerized polyether glycol of THF and neopentyl glycol as described in Example 8 (measured at 400 MHz by means of JEOL JNM-GX 400 NMR device); and

10 10 Fig. 6 shows  $^1\text{H-NMR}$  spectrum of a copolymerized polyether glycol of THF and bis-(2-hydroxyethyl)-n-butyl-amine as described in Example 13 (measured at 200 MHz by means of JEOL FX 200 NMR device).

#### DISCLOSURE

The present invention provides a process for  
15 producing a polyether polyol with a content of 0.5 to 99.5 % by weight of oxytetramethylene groups derived from tetrahydrofuran by copolymerizing tetrahydrofuran with a polyhydric alcohol having two or more hydroxyl groups per one molecule or by copolymerizing a mixture  
20 of tetrahydrofuran and another cyclic ether copolymerizable therewith with a polyhydric alcohol having two or more hydroxyl groups per one molecule with the use of a heteropoly-acid and/or its salt as a catalyst, which comprises allowing 0.1 to 15 molecules of water per one  
25 heteropoly-anion to exist in the catalyst phase, and also provides a novel polyether glycol synthesized by the above process.

The present invention relates to a new reaction, wherein a copolymerization proceeds only with THF  
30 and a polyhydric alcohol, and the presence of polyhydric alcohol residues in the resultant polyetherglycol is not limited to the ends of molecule but can also be contained within

the molecule. Further, in the present invention, water is not required to be added as a starting material in the reaction system, and no hydrolysis with addition of water is required to be conducted after the reaction, 5 but the terminal ends can directly be converted to OH groups. In addition, the catalyst can be recycled for reuse. Thus, the present invention possess such new specific features, which have not been realized in the prior art.

10 Such a polymerization as described above has surprisingly been accomplished for the first time by using a heteropoly-acid as a catalyst and allowing 0.1 to 15 molecules of water per one heteropoly-anion to exist in the catalyst phase.

15 Generally, in the copolymerization reaction of THF and a cyclic ether known in the art, in addition to the disadvantage of limited species of cyclic ethers which can be adopted, a polymerization is liable to proceed rather as a block polymerization due to the 20 difference in polymerization reactivity between THF and the cyclic ether, whereby the drawback is involved that a polyetherglycol low in crystallinity, which is preferable as a soft segment for an elastomer, can be obtained with difficulty. For example, tetrahydropyran 25 which is a 6-membered cyclic ether cannot be copolymerized, and oxepane which is a 7-membered cyclic ether is also known to be very low in copolymerizability with THF. On the contrary, the reactivities of 3-membered or 4-membered cyclic ethers such as ethylene oxide or 30 oxetane are extremely large as compared with THF, and therefore products in which ethylene oxide or oxetane are subjected to block polymerization are liable to be obtained.

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Whereas, according to the process of the present invention, various kinds of polyhydric alcohols can be adopted as a comonomer with THF, and besides a copolymer can be obtained in which the comonomer is incorporated randomly in the polymeric chain. Most of these copolymers have lower melting points than PTMG having the same molecular weight and are lower in crystallinity, and they can be expected to exhibit excellent elastic recovery even at lower temperatures, when utilized as soft segments for an elastomer.

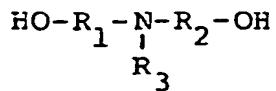
As the alcohols having two or more hydroxyl groups in one molecule to be used in the present invention, any alcohol may be available, provided that it has no substituent which interferes with the activity of the catalyst of the present invention. Preferable polyhydric alcohols may include dihydroxyalkanes such as ethylene glycol, propylene glycol, 1,3-propane diol, 1,4-butane diol, 1,3-butane diol, 2-methyl-1,3-propane diol, 1,5-pentane diol, 1,6-hexane diol, neopentyl glycol, 2-methyl-1,4-butane diol, hexane diol, heptane diol and the like; trihydroxyalkanes such as trihydroxyheptane, trihydroxyoctane, glycerine and the like; polyalkylene glycols such as diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol and the like. Among the polyhydric alcohols as mentioned above, dihydric alcohols are particularly preferred.

As the polyhydric alcohol, low molecular weight polymers of the polyether polyol derived by the process of the present invention using the polyhydric alcohol as exemplified above can also be used. Further, low molecular weight polymers of PTMG may be used as a part of the polyhydric alcohol. The low molecular weight polymer as herein mentioned is not particularly limited, so long as it has a molecular weight lower than the polymer to be synthesized, but for instance it

should preferably have a number average molecular weight within the range of from 100 to 500, when a polymer having a number average molecular weight of 600 or higher is to be synthesized, while a number average 5 molecular weight within the range of from 100 to 1,000 when a polymer having a number average molecular weight of 1,200 or more is to be synthesized. A use as a reactant material for polymerization by recycling an oligomer separated by extraction or distillation from 10 the polyether polyol synthesized according to the reaction of the present invention is a preferable example of using the above-described low molecular weight polymer in the reaction. Such a low molecular weight polymer may be added preferably in an amount of 15 10 wt. % or less in the starting monomer.

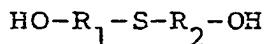
By allowing a monohydric alcohol as the alcohol to exist in the reaction system, an alkoxy group can be introduced into the polymer at its terminal ends.

As an polyhydric alcohol, it is also possible 20 to use a nitrogen containing polyhydric alcohol having a moiety comprising a secondary amine or a tertiary amine or a salt thereof in the molecule, and in this case a polymer containing nitrogen is obtained. The above nitrogen containing polyhydric alcohol is not particularly limited, but a compound having each one 25 hydroxyl group in the two substituents on the nitrogen atom is preferable, since it can give a polyetherglycol containing nitrogen atoms in the main chain, which can preferably be used as the starting material for elastomers. A preferable example of the nitrogen containing 30 polyhydric alcohol has the following structural formula:



[wherein R<sub>1</sub> and R<sub>2</sub> are selected from the group consisting of -(CH<sub>2</sub>)<sub>n</sub>- (wherein n: 2 - 10), -CH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>CH<sub>2</sub>- and -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, and R<sub>3</sub> is selected from the group consisting of hydrogen atom and 5 alkyl groups having 1 to 10 carbon atoms] such as diethanolamine and N-methyl-diethanolamine.

Alternatively, the polyhydric alcohol may also be a polyhydroxysulfide having sulfur atoms in the molecule. In this case, a polymer containing sulfur is 10 obtained. The polyhydroxysulfide is not particularly limited, and a preferable example is shown by the structural formula:



[wherein R<sub>1</sub> and R<sub>2</sub> are selected from the group consisting of -(CH<sub>2</sub>)<sub>n</sub>- (wherein n: 2 - 10), -CH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>CH<sub>2</sub>- and -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-] such as 2,2'-thiodiethanolamine and 3,3'-thiodipropanolamine.

If the above nitrogen containing polyhydric alcohol or polyhydroxyalkylenesulfide exists in the 20 reaction system in an amount of the 4-fold molar amount of the heteropoly-anion, polymerization activity will be lowered and hence it is preferable to use the above compounds in an amount less than the 4-fold molar amount of the heteropoly-anion.

25 The cyclic ether to be used in the present invention may include 3-membered cyclic ethers such as ethylene oxide, propylene oxide, isobutylene oxide, epichlorohydrin and the like; 4-membered cyclic ethers such as oxetane, 3,3-dimethyloxetane, 3-methyloxetane, 30 3,3-bis(chloromethyl)-oxetane and the like; 5-membered cyclic ethers such as methyl tetrahydrofuran, 1,3-dioxorane and the like; 6-membered cyclic ethers such as

trioxane and derivatives thereof; 7-membered cyclic ethers such as oxepane and derivative thereof; bicyclic 5-membered ethers such as 1,4-epoxycyclohexane and the like; large cyclic ethers such as 15-crown-3,20-crown-4, etc.; and oligomeric cyclic ethers which are polymers of THF or copolymers of THF and alkylene oxide.

The composition of the starting materials for the process of the present invention is not particularly limited, but comprises preferably 0.5 to 99.9 wt. % of THF, more preferably 10 to 99 wt. %. When THF is co-polymerized with both of a polyhydric alcohol and a cyclic ether other than THF, the proportions of the polyhydric alcohol and the cyclic ether other than THF in the starting materials are not particularly limited, but the polyhydric alcohol may preferably be used in an amount of two-fold moles or more of the cyclic ether other than THF.

The heteropoly-acid and its salt in the present invention refers comprehensively to oxy acids formed by condensation of at least one oxide of Mo, W and V with oxy acids of other elements such as P, Si, As, Ge, B, Ti, Ce, Co, etc. and salts of the oxy acids, the atomic ratio of the former to the latter being 2.5 to 12.

Examples of these catalysts may include 12-molybdophosphoric acid, 5-molybdo-2-phosphoric acid, 12-tungstophosphoric acid, 12-molybdotungstophosphoric acid, 6-molybdo-6-tungstophosphoric acid, 12-molybdo-vanadophosphoric acid, 11-molybdo-1-vanadophosphoric acid, 12-molybdotungstovanadophosphoric acid, 12-tungstovanadophosphoric acid, 12-molybdoniobo-phosphoric acid, 12-tungstosilicic acid, 12-molybdo-silicic acid, 12-molybdotungstosilicic acid, 12-molybdo-tungstovanadosilicic acid, 12-tungstoboric acid,

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- 12-molybdoboric acid, 12-molybdotungstoboric acid,  
 12-molybdovanadoboric acid, 12-molybdotungstovanadoboric  
 acid, 9-molybdonickelic acid, 6-molybdocobaltic acid,  
 6-tungstocobaltic acid, 11-molybdoarsenic acid,  
 5 12-tungstoarsenic acid, 12-tungstogermanic acid,  
 18-tungsto-2-arsenic acid, 18-molybdo-2-phosphoric acid,  
 9-molybdophosphoric acid, 18-tungsto-2-phosphoric acid,  
 12-titanomolybdic acid, 12-ceriomolybdic acid,  
 18-molybdo-2-phosphoric acid and salts thereof.

- 10 Among them, preferable examples include  
 12-molybdophosphoric acid, 18-molybdo-2-phosphoric acid,  
 9-molybdophosphoric acid, 12-tungstophosphoric acid,  
 18-tungsto-2-phosphoric acid, 11-molybdo-1-vanado-  
 phosphoric acid, 12-molybdotungstophosphoric acid,  
 15 6-molybdo-6-tungstophosphoric acid, 12-molybdotungsto-  
 vanadophosphoric acid, 12-tungstovanadophosphoric acid,  
 12-molybosilicic acid, 12-tungstosilicic acid,  
 12-molybdotungstosilicic acid, 12-molybdotungstovanado-  
 silicic acid, 12-tungstoboric acid, 12-molybdoboric  
 20 acid, 12-molybdotungstoboric acid, 12-molybdovanadoboric  
 acid, 12-molybdotungstovanadoboric acid, 12-tungsto-  
 germanic acid and 12-tungstoarsenic acid.

- The kinds of the salts are not particularly  
 limited. For example, there may be employed metal salts  
 25 of the metals belonging to the group I of the periodic  
 table such as Li, Na, K, Rb, Cs, Cu, Ag, Au, etc., of  
 the group II such as Mg, Ca, Sr, Ba, Zn, Cd, Hg etc., of  
 the group III such as Sc, La, Ce, Al, Ga, In, etc., of  
 the group VIII such as Fe, Co, Ni, Ru, Pd, Pt, etc. and  
 30 other metals such as Sn, Pb, Mn, Bi, etc., or ammonium  
 salts, amine salts and others.

Typical examples of these salts may include  
 12-tungstophosphate-1-lithium ( $\text{LiH}_2\text{PW}_{12}\text{O}_{40}$ ),  
 12-tungstophosphate-2-lithium ( $\text{Li}_2\text{HPW}_{12}\text{O}_{40}$ ),

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- 12-tungstophosphate-1-sodium ( $\text{NaH}_2\text{PW}_{12}\text{O}_{40}$ ), 12-tungstophosphate-2-sodium ( $\text{Na}_2\text{HPW}_{12}\text{O}_{40}$ ), 12-tungstophosphate-2-potassium ( $\text{K}_2\text{HPW}_{12}\text{O}_{40}$ ), 12-tungstophosphate-2-cesium ( $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ ), 12-tungstophosphate-2-silver  
 5 ( $\text{Ag}_2\text{HPW}_{12}\text{O}_{40}$ ), 12-tungstophosphate-1-magnesium ( $\text{MgHPW}_{12}\text{O}_{40}$ ), 12-tungstophosphate-1-calcium ( $\text{CaHPW}_{12}\text{O}_{40}$ ), 12-tungstophosphate-1-zinc ( $\text{ZnHPW}_{12}\text{O}_{40}$ ),  
 12-tungstophosphate-1-nickel ( $\text{NiHPW}_{12}\text{O}_{40}$ ), 12-tungstosilicate-1-nickel ( $\text{NiHSiW}_{12}\text{O}_{40}$ ), 12-tungstosilicate-  
 10 2-lithium ( $\text{Li}_2\text{H}_2\text{SiW}_{12}\text{O}_{40}$ ), 12-tungstosilicate-2-silver ( $\text{Ag}_2\text{H}_2\text{SiW}_{12}\text{O}_{40}$ ), 12-tungstosilicate-1-magnesium  
 ( $\text{MgH}_2\text{SiW}_{12}\text{O}_{40}$ ), 12-tungstosilicate-1-aluminum  
 ( $\text{AlHSiW}_{12}\text{O}_{40}$ ), 12-tungstosilicate-2-indium  
 ( $\text{InHSiW}_{12}\text{O}_{40}$ ), 12-tungstosilicate-1-gallium  
 15 ( $\text{GaHSiW}_{12}\text{O}_{40}$ ), 12-molybdophosphate-1-lithium  
 ( $\text{LiH}_2\text{PMo}_{12}\text{O}_{40}$ ), 12-molybdophosphate-1-magnesium  
 ( $\text{MgHPMo}_{12}\text{O}_{40}$ ), 12-tungstophosphate-2-ammonium  
 (( $\text{NH}_4$ )<sub>2</sub> $\text{HPW}_{12}\text{O}_{40}$ ), 12-tungstosilicate-1-tetramethylamine  
 ( $\text{N}(\text{CH}_3)_4\text{H}_3\text{SiW}_{12}\text{O}_{40}$ ), 12-tungstophosphate-1-iron  
 20 ( $\text{FePW}_{12}\text{O}_{40}$ ), 12-tungstophosphate-1-bismuth ( $\text{BiPW}_{12}\text{O}_{40}$ ),  
 12-tungstophosphate-1-aluminum ( $\text{AlPW}_{12}\text{O}_{40}$ ), 12-tungstophosphate-1-chromium ( $\text{CrPW}_{12}\text{O}_{40}$ ), 12-tungstophosphate-1-gallium  
 ( $\text{GaPW}_{12}\text{O}_{40}$ ), 12-tungstophosphate-1-indium  
 ( $\text{InPW}_{12}\text{O}_{40}$ ) and the like. A mixture with heteropoly-  
 25 acid may also be employed. The heteropoly-acid salt may  
 be prepared by titrating an aqueous solution of a  
 heteropoly-acid with carbonates or nitrates of various  
 metals, ammonia, amines, etc., followed by evaporation  
 to dry.

30 These heteropoly-acids or salts thereof may  
 also be used as the catalyst in the reduced form  
 thereof.

In general, a heteropoly-acid or its salt exists in the state wherein 20 to 40 molecules of water  
 35 coordinated per one molecule thereof and however in this

state, it has no polymerization activity at all. Whereas, when the above catalyst is subjected to drying treatment to change its number of water molecules coordinated (the molar ratio of the water coordinated to the heteropoly-anion), for examination of polymerization activity, it has unexpectedly been found that polymerization activity appeared when the moles of water existing in the catalyst phased per one heteropoly-anion was reduced to not higher than 15, particularly not higher than 8, and, moreover, specific ability could be exhibited such that the polyhydric alcohol was also activated to form a copolymer with THF in which the residue of the polyhydric alcohol is also bonded to the inner part of the polymer chain. If the molar ratio of water to the heteropoly-anion existing in the catalyst phase is less than 0.1, the efficiency of terminal hydroxylation will become worsened, and therefore the above ratio is required to be within the range of from 0.1 to 15. Although slightly different depending on the heteropoly-acid or its salt employed and the composition of the starting materials, the catalyst in which water is allowed to co-exist in an amount within the above range will not generally be dissolved uniformly in the starting material solution in the polymerization system, but it exists as a catalyst liquid phase while forming two liquid phases with the starting material organic phase or as a solid phase. If the water content is increased greater than the above ratio, polymerization activity will disappear and the heteropoly-acid becomes homogeneously soluble in the starting material solution. More specifically, the polymerization system will generally form two liquid phases of a catalyst liquid phase and a starting material organic phase when water is allowed to exist at a ratio of 1 to 15 molecules per one heteropoly-anion. If the amount of water is reduced to less than the ratio of about 1, the catalyst becomes a solid phase. However, even when water exists at a

ratio of 1 to 15 molecules per one heteropoly-anion, some heteropoly-acid salts do not form a liquid phase but remain as a solid phase, or otherwise the catalyst may sometimes be dissolved homogeneously without forming  
5 two liquid phases if the polyhydric alcohol concentra-  
tion in the starting material is very high. When the above ratio is within the range from 1 to 8, there can be obtained a polyether polyol having a number average molecular weight of 600 to 3,500, which can preferably  
10 be used as a starting material for elastomers.

Polymerization activity and the molecular weight of the polymer obtained will vary depending on the molar ratio of water to the heteropoly-anion existing in the catalyst phase, and their relationship  
15 will also be changed depending on the sort of the catalyst employed. Accordingly, it is preferable to carry out the reaction with an optimum content of water which can easily be determined according to the respec-  
tive conditions and purposes.

20 In the present invention, the water allowed to exist in the catalyst phase is estimated to exist in the state of being coordinated to the catalyst, when the catalyst is a solid phase, while in the state of being coordinated to the catalyst or of being dispersed in the  
25 catalyst phase, when the catalyst is a liquid phase. In this specification, the number of coordinated water molecules is defined as the average number of water molecules coordinated per one heteropoly-anion, when the catalyst is a solid phase, while it is defined as the value of the total number of water molecules in the  
30 catalyst liquid phase divided by the number of existing heteropoly-anions, when the catalyst exists as a liquid phase.

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- The number of coordinated water molecules can be controlled by heating the heteropoly-acid or its salt to a high temperature lower than the decomposition temperature or maintaining it at reduced pressure at a relatively lower temperature. Since the decomposition temperature of the catalyst differs depending on the particular catalyst employed, the heating temperature will be determined depending on the catalyst, but it is generally within the range of from 100 °C to 320 °C. It is also possible to control the number of coordinated water molecules so as to be increased from more scarce state than is required by supplementing a necessary amount of water mixed into the starting material for polymerization such as THF.
- In the reaction, wherein a polyhydric alcohol is incorporated into the polymer chain through an ether linkage, water is formed and therefore polymerization activity will be lost if the content of water in the system exceeds 15-fold moles of the heteropoly-anion. Accordingly, it is necessary to determine the molar ratio of a polyhydric alcohol to be reacted relative to THF and relative to the catalyst so that the amount of coordinated water molecules will not exceed 15 by the water formed in the system in an amount larger than the amount consumed as the polymer ends. When it is desired to enhance further the molar ratio of an alcohol/THF, water can be removed by distillation or other methods to maintain the number of water molecules coordinated to the heteropoly-anion at not more than 15, whereby a ratio of copolymerization of the alcohol can be enhanced.

On the contrary, if the amount of water molecules is less than that consumed as the terminal ends of the polymer, the number of coordinated water molecules in the catalyst will be decreased with the

progress of the reaction, whereby the polymer obtained will be increased in molecular weight with elapse of time, and therefore it is preferred to carry out the reaction while controlling the content of water in the 5 catalyst phase at a constant level by addition of a polyhydric alcohol or water.

The amount of the catalyst employed is not particularly limited, but the polymerization rate is slow if the catalyst amount in the reactor is small, and 10 therefore it is used in an amount of 0.01 to 20-fold weight, preferably 0.1 to 3-fold weight, of the starting material.

When the reaction is carried out in a two-liquid phase system with a volume of the catalyst liquid 15 phase of 10 % or more, preferably 30 % or more, of the total liquid phase volume in the reactor, a polymer having a very sharp molecular weight distribution can be obtained after the reaction from the starting material organic phase. The mechanism in which a polymer with a 20 sharp molecular weight distribution is formed is not clearly understood, but it may be estimated to be due to the selective extracting function possessed by the two-liquid phase system which migrates polymers having a certain or higher levels of molecular weights selectively 25 to the starting material organic phase and makes polymers having molecular weight lower than the levels remain in the catalyst liquid phase. For this reason, if the ratio of the catalyst liquid phase occupied in the total liquid phase is lower, the selective extracting function through levels of molecular weight 30 of polymers by the two-liquid phase will be damaged to give no sharp moelcular weight distribution.

Also, the catalyst may be carried on a carrier capable of adsorbing a heteropoly-acid or its salt such as activated charcoal, silica alumina, alumina, etc. and used as a fixed bed or a fluidized bed. By using a  
5 carried catalyst, separation between the polymer obtained and the catalyst can very easily be done with the catalyst amount dissolved in the polymer phase being very small, whereby the purification steps can be simplified to a great extent. As a carrier, activated  
10 charcoal is particularly preferred for its great adsorptive force for heteropoly-acids and salts thereof.

The reaction materials and the like to be provided for polymerization should preferably be contain no impurity such as peroxides or others.

15 The reaction temperature should preferably be from -10 to 120 °C, particularly from 30 to 80 °C, since too high a temperature tends to lower polymerization degree and also from the view-point of polymer yield. The yield will abruptly be decreased if the temperature exceeds 120 °C. The reactivity is lower at a tempera-  
20 ture lower than - 10 °C.

25 The time required for the reaction, which may differ depending on the catalyst amount and the reaction temperature, is 0.5 to 50 hours. The reaction pressure may be either atmospheric, pressurized or reduced pressure.

30 In the process of the present invention, the reaction may be carried out while stirring a polyhydric alcohol and THF or a polyhydric alcohol, THF and a cyclic ether together with a catalyst having a pre-determined number of coordinated water molecules.

The reaction system may include those conventionally used, such as the tank system, the tower system, etc. Also, either batch system or continuous system may be practiceable.

- 5 After the reaction, the catalyst may be removed by filtration, when it is a solid phase, or by phase separation, when it is a liquid phase and separated into two phases, or by extraction, etc., when it is homogeneously dissolved, followed by removal of  
10 unreacted monomers by distillation, etc., whereby the polyether polyol can be obtained. The polymer obtained is purified by washing or treatment with adsorbents, etc. to provide a commercial product. The catalyst may be used repeatedly as such, or after readjustment of the  
15 number of coordinated water molecules, if desired.

The composition of the copolymer can be varied within the range of from 0.5 to 99.5 wt. % of the content of oxytetramethylene groups derived from THF. The preferable composition of the copolymer for use as the  
20 starting material for elastomers such as polyurethane elastomers comprises 10 to 99.5 wt. % of the content of oxytetramethylene groups, more preferably 50 to 98 wt. %, particularly preferably 70 to 95 wt. %. When a copolymer contains oxytetramethylene groups in excess of  
25 99.5 wt. %, substantial difference thereof in physical properties and chemical properties from PTMG which is the homopolymer of THF will become very small.

When an alkylene glycol having 5 or more carbon atoms such as 1,5-pentane diol or 1,6-hexane diol  
30 is used as a polyhydric alcohol, a polyether glycol can be obtained, comprising the constituent unit represented by the formula (I) shown below and the constituent unit represented by the formula (II) shown below, with both ends of the molecule being hydroxyl groups:

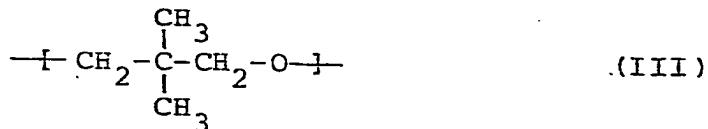
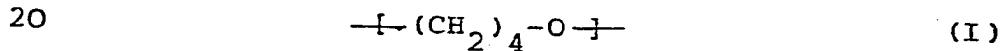
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(wherein n is an integer of 5 or more).

A polyetherglycol wherein the molar ratio of  
 5 the unit (I) to the unit (II) is 99:1 to 5:1, having a  
 number average molecular weight of 500 to 10,000 is a  
 polyether glycol which can preferably be used as soft  
 segments for an elastomer such as polyurethane, poly-  
 ester, polyamide, etc. Above all, a polymer wherein the  
 10 molar ratio of the unit (I) to the unit (II) is 50:1 to  
 5:1, having a number average molecular weight of 500 to  
 3,500 is particularly preferable as soft segments for an  
 elastomer.

When neopentyl glycol is used as a polyhydric  
 15 alcohol, a polyether glycol can be obtained, comprising  
 the constituent unit represented by the formula (I)  
 shown below and the constituent unit represented by the  
 formula (III) shown below, with both ends of the  
 molecule being hydroxyl groups:



A polyetherglycol wherein the molar ratio of  
 25 the unit (I) to the unit (III) is 99:1 to 5:1, having a  
 number average molecular weight of 500 to 10,000 and a  
 melting point of 18 °C or lower, is a polyether glycol

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- which is hard to crystallize even when the polymer has high molecular weight, and therefore can preferably be used as soft segments for an elastomer such as polyurethane, polyester, polyamide, etc. The elastomer 5 employing this polyetherglycol as soft segments exhibits excellent elastic recovery even at lower temperatures. Its number average molecular weight is preferably 500 to 3,500.

- On the other hand, when a nitrogen-containing 10 alcohol having a moiety comprising a secondary amine or a tertiary amine or a salt thereof in the molecule, a polyether polyol containing nitrogen can be obtained. When a compound having the formula shown below is used as the polyhydric alcohol containing nitrogen:



- [wherein  $\text{R}_1$  and  $\text{R}_2$  are selected from the group consisting of  $-(\text{CH}_2)_n-$  (wherein n: 2 - 10),  $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$  and  $-\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-$ , and  $\text{R}_3$  is selected from the group consisting of hydrogen atom and alkyl groups having 1 to 10 carbon atoms], a polyether glycol comprising the constituent unit represented by the following 20 formula (I) shown below and the constituent unit represented by the following formula (IV) shown below, with both ends of the molecule being hydroxyl groups, can be obtained:



[wherein  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are respectively the same as described above].

A polyetherglycol with a molar ratio of the unit (I) to the unit (IV) of 99:1 to 5:1, having a number average molecular weight of 500 to 10,000, is a polyether glycol, which can preferably be used as soft segments for an elastomer such as polyurethane, polyester, polyamide, etc. Its number average molecular weight is preferably 500 to 3,500. Polyetherglycols and elastomers synthesized by using these as a starting material are generally known to be deteriorated such as 5 yellow discoloration or lowering in strength, when exposed to oxygen,  $\text{NO}_x$  gas, light, heat, etc. As a method for preventing such deterioration, it has generally been practiced to incorporate a stabilizer such as a phenolic compound, an amine compound, a sulfur 10 compound, etc. However, such methods involved the drawbacks such that the amount of the stabilizer employed is limited due to compatibility with the polymer, that the stabilizer added may bleed out on the polymer surface to reduce the effect of the stabilizer, 15 etc. The polyurethane synthesized by using a nitrogen-containing polyetherglycol as described above will scarcely been discolored to yellow even when exposed to  $\text{NO}_x$  gas and also has the specific feature of excellent dyeing property. This is because amine structures are 20 incorporated into the molecule and the excellent dyeing property may be considered to be due to the presence of 25 amine structures in the soft segment.

A polyether polyol containing sulfur obtained when employing a polyhydroxyalkylsulfide as the 30 polyhydric alcohol is very stable even when exposed to oxygen, light, heat, etc. and also preferably used as soft segments for an elastomer such as polyurethane, polyester, polyamide, etc. Its number average molecular weight is preferably 500 to 3,500.

According to the present method, various polyhydric alcohols can be copolymerized with THF, and further polyhydric alcohols are copolymerized randomly within the chains formed by ring opening polymerization 5 of THF. Accordingly, most of the polyether polyols obtained are lower in crystallinity as compared with PTMG, and the elastomers by using these as soft segments can be expected to exhibit excellent resilient recovery even at low temperatures. Also, according to the 10 present method, it is possible to introduce amino groups or sulfur atoms into the polymer chains to synthesize polyalkylene ether polyols having yellow discoloration resistance and heat resistance not found in PTMG.

Further, according to the present method, 15 additional advantages unknown in the prior art can be obtained such that polyalkylene ether polyols can be synthesized in one step without requiring the hydrolysis step and that the catalyst employed can be used repeatedly.

20 The present invention is described in more detail by referring to the following Examples.

Example 1

Into a vessel equipped with a stirring means and a reflux condenser were charged 200 g of THF containing 350 ppm of H<sub>2</sub>O and 8.5 g of ethylene glycol. Then, 100 g 5 of tungstophosphoric acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) heated at 300 °C for 3 hours to be made anhydrous was added thereto (the moles of ethylene glycol were about 4-fold of the moles of tungstophosphoric acid, and the amount of water produced when the whole ethylene glycol is copolymerized is 4-fold 10 moles of tungstophosphoric, if the amount consumed as the terminal OH groups is not reckoned into calculation). By setting the temperature at 60 °C, stirring was continued in a nitrogen atmosphere for 4 hours, and the mixture was left to stand at room temperature to be separated into two 15 phases. From the upper layer, unreacted THF was removed by distillation to obtain 42 g of a transparent and viscous polymer.

The polymer obtained was found to have a number average molecular weight of 1500 as the result of measurement by gel permeation chromatography (GPC). The polymer had a melting point of 14 °C as measured by a differential scanning calorimeter (PERKIN-ELMER DSC-2) (at a temperature elevation speed of 4 °C/min.), which was lower by about 20 10 °C as compared with the PTMG having the same molecular weight. The <sup>1</sup>H-NMR spectrum (400 MHz) of the polymer obtained is shown in Fig. 1, in which the axis of abscissa indicates the chemical shift (ppm) when employing tetra-methylsilane as a standard substance. As the result of 25 detailed analysis, it was found that the polymer was a polyether glycol formed by a copolymerization of ethylene glycol and THF at a molar ratio of ethylene glycol/THF being 1/9, and the ratio of oxydimethylene groups existing at the ends of the molecule to those in the molecular 30 chain was 26:74.

Also, the  $^{13}\text{C}$ -NMR spectrum of the polymer obtained of which hydroxyl groups at both ends were acetylated is shown in Fig. 2, in which the axis of abscissa indicates the chemical shift (ppm) when employing tetramethylsilane 5 as a standard substance. When oxydimethylene groups exist consecutively from the terminal end, the carbon at the  $\beta$ -position of the terminal acetyl group ( $\text{CH}_3\text{--C(=O)--CH}_2\text{--CH(O--CH}_2\text{--O--C(=O)}$ )

exists at the position of  $\delta$  69.1 ppm, but the carbon at the  $\beta$ -position of the terminal acetyl group in 10 this polymer exists at  $\delta$  68.5 ppm, thus indicating that they are not units existing consecutively from the terminal end. It can be estimated from the above results that ethylene glycol was not copolymerized in blocks but randomly.

#### 15. Example 2

Polymerization was carried out by using the continuous polymerization device as shown in Fig. 3. First, into a polymerization tank 1 having a volume of 300 ml and having a stirring means and a reflux condenser was charged 200 g 20 of tungstophosphoric acid having a coordinated water number of 3.5 ( $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 3.5\text{H}_2\text{O}$ ). 150 g of a monomer mixture containing THF and a predetermined amount of diols as indicated in Table 1 was added thereto and the mixture was stirred. By setting the polymerization tank tempera- 25 ture at 60 °C, stirring was continued in a nitrogen atmosphere for 4 hours and feeding of the mixture con- taining THF and a predetermined amount (see Table 1) of diols was commenced at the rate of 32 ml/Hr. The mixture in the polymerization tank was delivered to a phase 30 separation tank 2, and the upper layer separated was removed by allowing it to be overflowed, and the catalyst phase of the lower layer was returned to the polymerization tank, wherein the reaction was carried out again. Thus,

continuous running was carried out for 100 hours. From the upper phase liquid overflowed, unreacted THF was removed by distillation at the distillation tower 3 to obtain a polymer. All the polymers were found as a result 5 of analysis to be polyether glycol having OH groups at both ends in which one molecule of diols on an average in one molecule of polymer was randomly copolymerized. The compositions of the starting materials when employing various kinds of diols and the results were shown in 10 Table 1.

The  $^1\text{H}$ -NMR spectrum (measured by JEOL JNM-GX400 nuclear magnetic resonance apparatus) of the polyether glycol prepared by copolymerizing THF with 1,6-hexane diol is shown in Fig. 4, in which the axis of abscissa indicates the chemical shift (ppm) when employing tetramethyl- 15 silane as a standard substance.

Table 1

Comonomer	Composition of starting material:	Polymer yield (%)	Number average molecular weight of polymer	Melting point *1) of polymer (°C)
	Diol			
Ethylene glycol	1.8	29	1600	16
1,3-Propane diol	1.35	34	1800	14
1,6-Hexane diol	1.65	31	1500	18
1,3-Butane diol	1.60	30	1700	15

\*1) measured by differential scanning calorimeter  
 (PERKIN-ELMER DSC-2 Model) at a temperature elevating  
 speed of 4 °C/min.

Example 3

Into a vessel equipped with a stirring means and a reflux condenser were charged 200 g of THF containing 350 ppm of H<sub>2</sub>O and 10.6 g of 1,3-propane diol. Then, each 5 of 100 g of the catalysts made to anhydrous state as indicated in Table 2 was added thereto. At a temperature set at 60 °C, stirring was continued in a nitrogen atmosphere for 4 hours and the mixture was left to stand at room temperature to be separated into two phases. From 10 the upper layer, unreacted THF was removed by distillation to obtain a copolymer in which 1,3-propanol was copolymerized. The yields of the polymers obtained are shown in Table 2. The number of coordinated water in the catalysts during the reaction was within the range of from 0.5 to 4.

Table 2

	Catalyst	Polymer yield (g)
5	12-molybdo-1-phosphoric acid (H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> )	60
10	18-molybdo-2-phosphoric acid (H <sub>6</sub> P <sub>2</sub> Mo <sub>18</sub> O <sub>62</sub> )	18
15	12-tungsto-1-phosphoric acid (H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> )	51
20	18-tungsto-2-phosphoric acid (H <sub>6</sub> P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> )	35
25	12-tungsto-1-silicic acid (H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub> )	45
30	12-tungsto-1-germanic acid (H <sub>4</sub> GeW <sub>12</sub> O <sub>40</sub> )	48
	12-tungsto-1-boric acid (H <sub>5</sub> BW <sub>12</sub> O <sub>40</sub> )	31
	12-tungsto-1-arsenic acid (H <sub>3</sub> AsW <sub>12</sub> O <sub>40</sub> )	36
	11-molybdo-1-vanado-1-phosphoric acid (H <sub>4</sub> PMo <sub>11</sub> VO <sub>40</sub> )	43
	12-tungsto-1-phosphate-2-cesium (Cs <sub>2</sub> HPW <sub>12</sub> O <sub>40</sub> )	28
	12-tungsto-1-phosphate-1-aluminum (AlPW <sub>12</sub> O <sub>40</sub> )	35
	12-tungsto-1-phosphate-1-bismuth (BiPW <sub>12</sub> O <sub>40</sub> )	38
	12-tungsto-1-silicate-1-lithium (LiH <sub>3</sub> SiW <sub>12</sub> O <sub>40</sub> )	23
	12-tungsto-1-silicate-1-calcium (CaH <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub> )	17
	12-molybdo-1-phosphate-1-cesium (CsH <sub>2</sub> PMo <sub>12</sub> O <sub>40</sub> )	20

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12-molybdo-1-silicate-1-lithium (LiH <sub>3</sub> SiMo <sub>12</sub> O <sub>40</sub> )	21
12-tungsto-1-arsenate-1-lithium (LiH <sub>2</sub> AsW <sub>12</sub> O <sub>40</sub> )	18
12-tungsto-1-phosphate-1-indium (InPW <sub>12</sub> O <sub>40</sub> )	31
12-tungsto-1-phosphate-1-chromium (CrPW <sub>12</sub> O <sub>40</sub> )	33

5

Example 4 and Comparative example 1

Into a vessel equipped with a stirring means and a reflux condenser were charged 200 g of THF and 1,3-propane diol in amounts as indicated in Table 3. Then, 100 g of 5 tungstophosphoric acid controlled to a coordinated water number of 2 was added thereto. At a temperature set at 60 °C, stirring was continued in a nitrogen atmosphere for 4 hours and the mixture was left to stand at room temperature to be separated into two phases. From the upper 10 layer, unreacted THF was removed by distillation to obtain a polymer. The polymerization results and the number average molecular weights determined by GPC were shown in Table 3.

Table 3

	1,3-Propane diol (g)	1,3-Propane diol $H_3PW_{12}O_{40}$ (molar ratio)	Polymer yield (g)	Number average molecular weight of polymer
Example 4	5.3	2	48	1800
	10.6	4	23	1300
	15.9	6	6.5	600
Comparative example 1 *1)	47.7	18	trace	—

\*1) Substantial number of coordinated water molecules in the catalyst during the reaction was 15 or more.

Example 5

Polymerization was carried out by using the continuous polymerization device as shown in Fig. 3. First, into a 300 ml of polymerization tank 1 having a stirring means and a reflux condenser was charged 200 g of 12-tungstophosphoric acid having a coordinated water number of 3.5 ( $H_3PW_{12}O_{40} \cdot 3.5H_2O$ ). 150 g of a monomer mixture containing THF and 1.8 wt. % of 1,4-butane diol was added thereto, and the mixture was stirred. By setting the polymerization tank temperature at 60 °C, stirring was continued in a nitrogen atmosphere for 4 hours and feeding of a mixture containing THF and 1.8 wt. % of 1,4-butane diol was commenced at the rate of 32 ml/Hr. The reaction was carried out while circulating the liquid from the lower layer in the phase separation tank 2 to the reaction tank and removing the upper layer after phase separation by allowing it to overflow. From the upper layer liquid overflow, unreacted THF was removed by distillation to obtain PTMG. Substantially no unreacted 1,4-butane diol was detected. After continuous running for 100 hours, 850 g of PTMG having a number average molecular weight of 1750 was obtained.

Example 6

Into a vessel equipped with a stirring means, 100 g of THF with a water content of 350 ppm, 3 g of 1,4-butane diol and 6 g of a PTMG oligomer having a number average molecular weight of 600 were added. Then, 50 g of 12-tungstosilicate-l-lithium ( $LiH_3SiW_{12}O_{40}$ ) was added thereto. The vessel was sealed up and stirring was continued at 60 °C in a nitrogen atmosphere for 6 hours. After the reaction, the mixture was left to stand to be separated into two liquid phases, and the catalyst phase of the lower layer was separated. From the upper phase,

unreacted THF was removed by distillation to obtain 31 g of PTMG having a number average molecular weight of 1800.

Example 7

Into a vessel equipped with a stirring means and a  
5 reflux condenser, 200 g of THF containing 350 ppm of H<sub>2</sub>O,  
8.0 g of propylene oxide and 13 g of 1,4-butane diol were  
charged. Then, 100 g of tungstophosphoric acid  
(H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) made to anhydrous state by heating at 300 °C  
for 3 hours was added thereto. By setting the temperature  
10 at 60 °C, stirring was continued in a nitrogen atmosphere  
for 4 hours, and then the mixture was left to stand at  
room temperature to be separated into two phases. From  
the upper phase, unreacted THF was removed by distillation  
to obtain 49 g of a transparent and viscous polymer. The  
15 polymer obtained, as a result of analysis, was found to be  
a polyalkylene ether glycol, having OH groups at both  
ends, with two molecules of propylene oxide being copoly-  
merized on an average in one molecule. The number average  
molecular weight was measured by GPC to be 1500.

20 Example 8

By means of a continuous polymerization device as  
shown in Fig. 3, polymerization was carried out. First,  
into a polymerization tank 1 having a volume of 10 liter  
and having a stirring means and a reflux condenser, 3.0 Kg  
25 of THF containing 200 ppm of water and 1.8 wt. % neopentyl  
glycol was charged. While stirring the mixture, 8.0 Kg of  
tungstophosphoric acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) made anhydrous by  
heating at 300 °C was added thereto to prepare a catalyst  
liquid phase. The catalyst liquid phase has a volume of  
30 about 6.3 liter. Then, by setting the temperature at  
60 °C, THF containing 200 ppm of water and 1.8 wt. % of  
neopentyl glycol was fed into the vessel at a rate of one

liter/hour. The liquid in the polymerization tank overflown was subjected to phase separation in the phase separation tank 2, and polymerization was carried out, while withdrawing the starting material organic phase of 5 the upper phase continuously and returning the catalyst liquid phase into the polymerization tank. From the starting material organic phase, unreacted THF was recovered by vacuum distillation to obtain 27.8 Kg of a polymer. The polymer was analyzed to find that it was a 10 polyalkylene ether glycol, having OH groups at both ends, with one molecule of neopentyl glycol randomly copolymerized on an average per one molecule of the polymer. The number average molecular weight was found to be 1970, with the molecular weight distribution ( $\bar{M}_{vis}/\bar{M}_n$ ) being 15 1.58. Here,  $\bar{M}_n$  is the number average molecular weight determined by quantifying OH groups, and  $\bar{M}_{vis}$  is a viscosity average molecular weight and calculated from the following formula correlated with the viscosity measured at 40 °C:

20 
$$\bar{M}_{vis} = \text{antilog } (0.493 \log \text{viscosity(cp)} + 3.0646).$$

In the Examples shown below, unless otherwise noted, the molecular weight distribution ( $\bar{M}_{vis}/\bar{M}_n$ ) was determined according to the above method.

This polymer was found to have a melting point of 25 10 °C, as a result of measurement by means of a differential scanning calorimeter (PERKIN-ELMER DSC-2 MODEL) (measured at a temperature elevation speed of 4 °C/min.). The  $^1H$ -NMR spectrum of this polymer is shown in Fig. 5, wherein the axis of abscissa shows the chemical shift (ppm) 30 when employing tetramethylsilane as a standard substance.

Example 9 and Comparative example 2

Into a vessel equipped with a stirring means and a reflux condenser were charged 200 g of THF containing 100 ppm of H<sub>2</sub>O and 4.2 g of ethylene glycol. To this mixture was added 100 g of tungstophosphoric acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·nH<sub>2</sub>O) controlled to a certain number of coordinated water by heating at a temperature of 150 to 250 °C for 0.5 to 2 hours. After stirring was continued at 60 °C in a nitrogen atmosphere for 4 hours, the mixture was left to stand at room temperature to be separated into two phases. From the upper layer, unreacted THF was removed by distillation to obtain a copolymerized polyether glycol of ethylene glycol and THF. The polymerization results are shown in Table 4. The number average molecular weights were measured by GPC.

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Table 4

	Water in catalyst phase (mol)	Form of polymerization system	Polymer	
			Yield (%)	Number average molecular weight
Example 9	3	Two-liquid phase	24	1950
	5	do	15	1350
	8	do	3.5	800
	10	do	1.0	600
Comparative example 2	18	Homo-geneous phase	trace	—
	30	do	trace	—

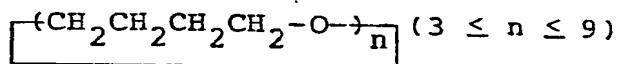
Example 10

A vessel equipped with a stirring means was charged with 100 g of THF containing 30 ppm of water, 2 g of 1,3-propane diol and 5 g of a low molecular weight polymer of a polyether polyol (number average molecular weight: 600) wherein 1,3-propane diol and THF are copolymerized at a molar ratio of 1:8. Subsequently, 50 g of tungstosilicic acid ( $H_4SiW_{12}O_{40} \cdot 2H_2O$ ) controlled to a coordinated water number of 2 was added to the mixture.

Stirring was continued at 60 °C in a nitrogen atmosphere for 6 hours. After the reaction, the mixture was left to stand at room temperature to be separated into two liquid phases, from which the catalyst layer of the lower phase was separated. Unreacted monomer was removed by distillation from the upper phase to obtain 30 g of a polyether glycol having a number average molecular weight of 1750. Additionally, substantially no unreacted 1,3-propan diol would be detected, and accordingly it can be estimated that all of 1,3-propane diol has copolymerized.

Example 11

A vessel equipped with a stirring means was charged with 100 g of THF containing 30 ppm of water, 2 g of 1,3-propane diol, 5 g of a low molecular weight polymer of a polyether polyol (number average molecular weight: 600) wherein 1,3-propane diol and THF are copolymerized at a molar ratio of 1:8 and 2 g of an oligomeric cyclic ether of the formula:



Subsequently, 50 g of tungstosilicic acid ( $H_4SiW_{12}O_{40} \cdot 2H_2O$ ) controlled to a coordinated water number of 2 was added to the mixture. Stirring was

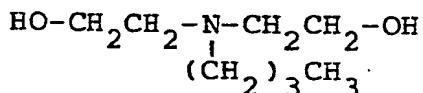
continued at 60 °C in a nitrogen atmosphere for 10 hours. After the reaction, the mixture was left to stand at room temperature to be separated into two liquid phases. Unreacted monomer was removed by distillation from the upper phase to obtain 35 g of a polyether glycol having a number average molecular weight of 2000. This polymer phase was found to contain 0.15 g of the oligomeric cyclic ether, and the catalyst phase contained 0.1 g of the same cyclic ether. From this result, the most of oligomeric cyclic ether may be estimated to be copolymerized into the polymer. Additionally, substantially no unreacted 1,3-propane diol could be detected, and accordingly it can be estimated that all of 1,3-propane diol has copolymerized.

#### Example 12

In 100 g of THF was dissolved 10 g of tungstophosphoric acid with a coordinated water number of 30( $H_3PW_{12}O_{40} \cdot 30H_2O$ ). Then, 50 g of granular activated charcoal was added to the solution, followed by mixing at room temperature for one hour. The activated charcoal was filtered, dried and heated at 300 °C for 3 hours to obtain a carried catalyst. The above carried catalyst in an amount of 50 g, 160 g of THF containing 50 ppm of  $H_2O$  and 1.0 g of ethylene glycol were charged into a air-tight stainless steel vessel. After displaced with nitrogen gas, the vessel was hermetically sealed, and shaking was continued for 24 hours on a shaking machine set at 60 °C. Next, the catalyst carried on activated charcoal was separated by filtration, and unreacted monomer was removed by distillation from the filtrate to obtain 12 g of a polyether glycol in which ethylene glycol and THF were copolymerized.

Example 13

A vessel equipped with a stirring means and a reflux condenser was charged with 200 g of THF containing 350 ppm of H<sub>2</sub>O and 11.2 g of bis-(2-hydroxyethyl)-n-butylamine:



Then, 100 g of tungstophosphoric acid made anhydrous by heating at 300 °C for 3 hours (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) was added thereto. Stirring was continued at 60 °C in a nitrogen atmosphere for 6 hours. The reaction mixture was in a state of two liquid phases, and left to stand after the reaction at room temperature to be separated into two phases. From the upper phase, unreacted THF was removed by distillation to obtain 60.3 g of a transparent and viscous polymer. As a result of elemental analysis and <sup>1</sup>H-NMR measurement of the polymer obtained, the polymer was found to be a polyether glycol copolymerized at a ratio of bis-(2-hydroxyethyl)-n-butylamine and THF being 1/25. The <sup>1</sup>H-NMR spectrum of the polymer is shown in Fig. 6, wherein the axis of abscissa shows the chemical shift (ppm) when employing tetramethylsilane as a standard substance. Also, the polymer obtained was found to contain substantially no unreacted bis-(2-hydroxyethyl)-n-butylamine, as confirmed by gas chromatography. As the result of measurement of the molecular weight of the polymer by gel permeation chromatography, the number average molecular weight was found to be 1700.

Example 14

Various amines as indicated in Table 5 were charged together with 200 g of THF containing 350 ppm of H<sub>2</sub>O

into a vessel equipped with a stirring means and a reflux condenser. Then, 100 g of tungstophosphoric acid made anhydrous by heating at 300 °C for 3 hours (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) was added thereto. After stirring was continued at 60 °C in a nitrogen atmosphere for 6 hours, the mixture was left to stand to be separated into two phases. From the upper phase, unreacted THF was removed to obtain a polymer in which amine was copolymerized with THF. Table 5 shows the kind of amines and the composition of starting materials charged, the polymer yield after the reaction and the nitrogen content in the polymer obtained.

Table 5

	Amine $R_1$ $R_2-N-R_3$	Composition of starting material: Amine Amine + THF (wt.%)	Polymer yield (%)	Nitrogen content in polymer (wt.%)
5	$R_1 = -C(CH_3)_3$ $R_2 = -CH_2CH_2CH_2CH_2OH$ $R_3 = -CH_2CH_2OH$	6.2	64	0.9
10	$R_1 = -CH_3$ $R_2 = -CH_2CH_2OH$ $R_3 = -CH_2CH_2OH$	3.9	57	0.6
15	$R_1 = -CH_2CH_2CH_2CH_3$ $R_2 = -CH_2CH_2CH_2CH_2OH$ $R_3 = -CH_2CH_2CH_2CH_2OH$	7.0	56	0.7
20	$R_1 = -C(CH_3)_3$ $R_2 = -CH_2CH_2CH_2OH$ $R_3 = -CH_2CH_2CH_2OH$	6.2	60	1.0
25	$R_1 = -CH_2CH_2CH_2CH_3$ $R_2 = -CH(CH_3)CH_2OH$ $R_3 = -CH_2CH_2OH$	5.8	50	0.4
30	$R_1 = -CH_2CH_2OH$ $R_2 = -CH_2CH_2OH$ $R_3 = -CH_2CH_2OH$	5.9	39	0.5
	$R_1 = -CH_2CH_2CH_2CH_3$ $R_2 = -CH_2CH_2OH$ $R_3 = -CH_2CH_2-O-CH_2CH_2OH$	6.4	38	0.4
3Q	$R_1 = H$ $R_2 = -CH_2CH_2OH$ $R_3 = -CH_2CH_2OH$	3.5	59	0.8

Example 15

A vessel equipped with a stirring means and a reflux condenser was charged with 200 g of THF containing 350 ppm of H<sub>2</sub>O and 8.2 g of thiодиethanol  
5 [HO-CH<sub>2</sub>CH<sub>2</sub>-S-CH<sub>2</sub>CH<sub>2</sub>-OH]. Then, 100 g of tungsto-phosphoric acid made anhydrous by heating at 300 °C for 3 hours (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) was added thereto. Stirring was continued at 60 °C in a nitrogen atmosphere for 6 hours. The reaction mixture was in a state of two liquid  
10 phases, and after the reaction left to stand to be separated into two phases. From the upper phase, unreacted THF was removed by distillation to obtain 14 g of a transparent and viscous polymer. As a result of elemental analysis of the polymer by fluorescent X-ray  
15 and measurement of <sup>1</sup>H-NMR, the polymer was found to be a polyether glycol copolymerized at a molar ratio of thiодиethanol/THF being 1/22. Substantially no unreacted monomer was found to exist in the polymer obtained. As a result of measurement by gel permeation  
20 chromatographyhy (GPC), the polymer obtained was found to have a number average molecular weight of 2,000.

Example 16

Into a vessel equipped with a stirring means and a reflux condenser, 200 g of THF containing 350 ppm of H<sub>2</sub>O and various kinds of thioglycols as indicated in Table 6 were charged. Then, 100 g of tungstophosphoric acid made anhydrous by heating at 300 °C for 3 hours (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) was added thereto. Stirring was continued at 60 °C in a nitrogen atmosphere for 6 hours. The reaction mixture was in a state of two liquid phases, and after the reaction left to stand to be separated into two phases. From the upper phase, unreacted THF was removed by distillation to obtain a polymer in which a thioglycol and THF were copolymerized. Table 6 shows

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the kind of thioglycols, the composition of starting materials, and the polymer yield after the reaction.

Table 6

	Thioglycol $(R_1-S-R_2)$	Composition of starting material: Thioglycol [Thioglycol] + THF (wt.%)	Polymer yield (%)	Number average molecular weight of polymer (wt.%)
5	$R_1 = -CH_2CH_2CH_2CH_2OH$ $R_2 = -CH_2CH_2OH$	4.7	9	2800
10	$R_1 = -CH_2CH_2OCH_2CH_2OH$ $R_2 = -CH_2CH_2OH$	5.2	12	1800
15	$R_1 = -CH(CH_3)CH_2OH$ $R_2 = -CH_2CH_2OH$	5.0	8	1800
20	$R_1 = -CH_2CH_2SCH_2CH_2OH$ $R_2 = -CH_2CH_2OH$	5.6	3	2500

Example 16

Into a vessel equipped with a stirring means were charged 50 g of THF with a water content of 30 ppm, 1 g of 1,3-propane diol and 15 g of a low molecular weight 5 polymer (number average molecular weight: 600) of a polyether glycol prepared by copolymerization of 1,3-propane diol and THF at a molar ratio of 1:8.

As a next step, 50 g of tungstophosphoric acid ( $H_3PW_{12}O_{40} \cdot 1H_2O$ ) controlled to a coordinated water 10 number of 1 was added to the mixture, and the reaction was carried out under a nitrogen atmosphere at a temperature set at 60 °C for 20 hours. After the reaction, the mixture was added with 250 g of  $H_2O$  and 250 g of chloroform, and was mixed, followed by separation into 15 two phases. From the chloroform phase, unreacted monomers and chloroform were removed by vacuum distillation to obtain 25 g of a polymer. The polymer was analyzed to be a polyether glycol in which 1,3-propane diol and THF were copolymerized at a molar ratio of 1:8, 20 having a number average molecular weight of 1950. As a result of analysis of the polymer obtained by gel permeation chromatography (GPC), the low molecular weight polymer of polyether glycol added as the starting material was found to be consumed. Thus, it may be 25 estimated to be used in the copolymerization reaction with THF.

Application example 1

By using the starting materials of the copolymerized polyetherglycols as shown in Table 7 and PTMG as 30 Control, polyurethane films were prepared. Polyurethane was prepared by adding to the polyetherglycol, 1.55-fold mole thereof of 4,4'-diphenylmethane diisocyanate to synthesize a prepolymer, dissolving the prepolymer in

5-fold weight of the prepolymer of dimethylacetamide solvent and allowing the free isocyanate groups to react with equal moles of amines [a mixture of ethylenediamine and diethylamine; a molar ratio of diethylamine/5 ethylenediamine being  $\sqrt{0.064/1}$ ] at 70 °C for 3 hours. The polyurethane obtained had a molecular weight of about 70,000. The polyurethane was formed into a film with a thickness of 0.125 mm and a width of 1 mm and its low temperature recovery (recovery at 10 °C ten seconds 10 after release from elongation after the film had been elongated to 100 % at 10 °C for 16 hours) was measured. The results are shown in Table 7, which shows excellent 15 low temperature recovery of the copolymerized polyetherglycol as compared with the polyurethane film employing PTMG.

$\sqrt{0.0128/1}$

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Table 7

	Polyether glycol composition (molar ratio)	Number average molecular weight of polyether glycol <sup>*1)</sup>	Recovery <sup>*2)</sup> (%)
5	$\begin{array}{c} +(\text{CH}_2)_5-\text{O}\} / +(\text{CH}_2)_4-\text{O}\} \\ = 1/21 \end{array}$	2100	35
10	$\begin{array}{c} +(\text{CH}_2)_6-\text{O}\} / +(\text{CH}_2)_4-\text{O}\} \\ = 1/25 \end{array}$	1900	34
15	$\begin{array}{c} \text{CH}_3 \\   \\ +\text{CH}_2-\text{C}-\text{CH}_2-\text{O}\} / +(\text{CH}_2)_4-\text{O}\} \\   \\ \text{CH}_3 \\ = 1/28 \end{array}$	2150	81
20	Control data $\text{HO}+(\text{CH}_2)_4-\text{O}\}_{n\text{H}}$	1960	24

Foot Note: \*1) number average molecular weight by OH value measurement.

25 \*2) recovery at 10 °C 10 seconds after release from elongation after the film had been elongated at 10 °C to 100 % for 16 hours.

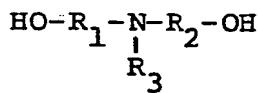
CLAIMS

1. A process for producing a polyether polyol having a content of 0.5 to 99.5 % by weight of oxytetramethylene groups derived from tetrahydrofuran by copolymerizing tetrahydrofuran with a polyhydric alcohol having two or more hydroxyl groups per one molecule with the use of a heteropoly-acid and/or its salt as a catalyst, characterized in that 0.1 to 15 molecules of water per one heteropoly-anion are present in the catalyst phase.
2. A process for producing a polyether polyol having a content of 0.5 to 99.5 % by weight of oxytetramethylene groups derived from tetrahydrofuran by copolymerizing a mixture of tetrahydrofuran and another cyclic ether copolymerizable therewith with a polyhydric alcohol having two or more hydroxyl groups per one molecule with the use of a heteropoly-acid and/or its salt as a catalyst, characterized in that 0.1 to 15 molecules of water per one heteropoly-anion are present in the catalyst phase.
3. A process according to either of the Claims 1 or 2, wherein the amount of water existing in the catalyst phase is within the range of from 1 to 8 molecules per one heteropoly-anion.
- 25 4. A process according to any of Claims 1 to 4, wherein the polyhydric alcohol is a dihydric alcohol having 2 to 10 carbon atoms.

5. A process according to Claim 4, wherein the dihydric alcohol is one or a mixture of two or more compounds selected from the group consisting of ethylene glycol, propylene glycol, 1,3-propane diol, 1,4-butane diol, 2-methyl-1,3-propane diol, 1,5-pentane diol, neopentyl glycol, 2-methyl-1,4-butane diol, hexane diol, heptane diol and octane diol.

6. A process according to any of the Claims 1 to 3, wherein the polyhydric alcohol has a moiety containing a secondary amine or a tertiary amine or salts thereof in its molecule..

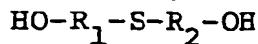
7. A process according to Claim 6, wherein the polyhydric alcohol having a moiety containing a secondary amine or a tertiary amine in its molecule has a structural formula:



wherein  $\text{R}_1$  and  $\text{R}_2$  are selected from the group consisting of  $-(\text{CH}_2)_n-$  (wherein n: 2 - 10),  
20  $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$  and  $-\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-$ , and  $\text{R}_3$  is selected from hydrogen atom and alkyl groups having 1 to 10 carbon atoms.

8. A process according to any of the Claims 1 to 3, wherein the polyhydric alcohol is a polyhydroxyalkyl sulfide.

9. A process according to Claim 8, wherein the polyhydroxyalkyl sulfide has the structural formula:



wherein R<sub>1</sub> and R<sub>2</sub> are selected from the group consisting of -(CH<sub>2</sub>)<sub>n</sub>- (wherein n is 2 - 10), -CH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>CH<sub>2</sub>- and -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-.

10. A process according to Claims 1 or 3, wherein a low  
5 molecular weight polymer of the polyether polyol  
obtained by copolymerizing tetrahydrofuran and the poly-  
hydric alcohol is used as at least a part of the poly-  
hydric alcohol.

11. A process according to Claim 2 or 3, wherein a low  
10 molecular weight polymer of the polyether polyol  
obtained by copolymerizing tetrahydrofuran, other cyclic  
ether copolymerizable therewith and the polyhydric  
alcohol is used as at least a part of the polyhydric  
alcohol, or an oligomeric cyclic ether obtained by co-  
15 polymerizing tetrahydrofuran, other cyclic ether co-  
polymerizable therewith and the polyhydric alcohol is  
used as at least a part of the cyclic ether.

12. A process according to any of Claims 1 to 11,  
wherein the polymerization system forms two-liquid  
20 phases of the organic phase of starting materials and  
the catalyst liquid phase, and the reaction is carried  
out in the two-liquid phase system in which the catalyst  
liquid phase exists at 10 vol. % or more of the total  
liquid phase in the reactor, followed after the reaction  
25 by phase separation to recover a polyether polyol from  
the organic phase of starting materials.

13. A process according to any of Claims 1 to 12,  
wherein the catalyst or the phase containing the  
catalyst is recovered by separation and used repeatedly  
30 for the polymerization reaction.

14. A process according to any of Claims 1 to 4,  
6, 8 and 10 to 13, wherein the catalyst is a

heteropoly-acid formed by condensation of at least one oxide selected from the group consisting of Mo, W and V and an oxy-acid of the element selected from the group consisting of P, Si, As, Ge, B, Ti, Ce and Co.

- 5        15. A process according to Claim 14, wherein the heteropoly-acid is one or a mixture of two or more compounds selected from the group consisting of 12-molybdo-phosphoric acid, 18-molybdo-2-phosphoric acid, 9-molybdophosphoric acid, 12-tungstophosphoric acid, 18-tungsto-2-phosphoric acid, 11-molybdo-1-vanadophosphoric acid, 12-molybdotungstophosphoric acid, 6-molybdo-6-tungstophosphoric acid, 12-molybdotungstovanadophosphoric acid, 12-tungstovanadophosphoric acid, 12-molybdosilicic acid, 12-tungstosilicic acid, 12-molybdotungstosilicic acid, 12-molybdotungstovanadosilicic acid, 12-tungstoboric acid, 12-molybdo-boric acid, 12-molybdo-tungstoboric acid, 12-molybdovanado-boric acid, 12-molybdotungstovanadoboric acid, 12-tungstogermanic acid and 12-tungstoarsenic acid.

- 20        16. A polyether glycol comprising the constituent unit represented by the formula (I) shown below and the constituent unit (II) shown below, with a molar ratio of the unit (I) to the unit (II) being 99:1 to 5:1, having a number average molecular weight of 500 to 10,000, with 25 the molecule being terminated at both ends with hydroxyl groups:



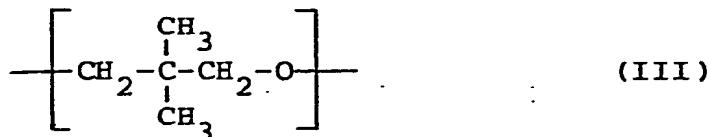
wherein n is an integer of 5 or more.

- 30        17. A polyether glycol comprising the constituent unit represented by the formula (I) shown below and the

constituent unit (III) shown below, with a molar ratio of the unit (I) to the unit (III) being 99:1 to 5:1, having a number average molecular weight of 500 to 10,000 and a melting point of 18 °C or lower, with the molecule being terminated at both ends with hydroxyl groups:



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18. A polyether glycol comprising the constituent unit represented by the formula (I) shown below and the constituent unit (IV) shown below, with a molar ratio of the unit (I) to the unit (IV) being 99:1 to 5:1, having a number average molecular weight of 500 to 10,000, with the molecule being terminated at both ends with hydroxyl groups:



20



25

wherein  $\text{R}_1$  and  $\text{R}_2$  are selected from the group consisting of  $-(\text{CH}_2)_n-$  (wherein n: 2-10),  $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$  and  $-\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-$ , and  $\text{R}_3$  is selected from the group consisting of hydrogen atom and alkyl groups having 1 to 10 carbon atoms.

19. A polyether glycol, obtainable by a process according to any of the Claims 1 to 15.

20. Polyurethane, comprising segments formed of a polyether glycol according to any of the Claims 16 to 19.

PATENTANWÄLTE  
STREHL SCHÜBEL-HOPF SCHÜLZ  
WIDENMAYERSTRASSE 17, D-8000 MÜNCHEN 22 0158229

DIPLO. ING PETER STREIL  
DIPLO.-CHEM. DR. URSULA SCHÜBEL-HOPF  
DIPLO.-PHYS. DR. RÜTERG SCHULZ  
AUCH RECHTSANWALT BEI DEN  
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Empfang bestätigt  
Rec'dt acknowledged 7th June 1985

The request for correction is allowed under  
R. 88 EPC ~~+ with the exception of the deleted~~  
~~points,~~ - 2 JUIL. 1985  
THE HÄGUE,  
RECEIVING SECTION. *Open*

Re.: Patent Application No. 85 103 690.5  
ASAHI KASEI KOGYO K.K.  
Our ref.: EPA-23 031

We enclose an amended page 45, in order to amend an obvious error on page 45, line 5 of the description.

The erroneously stated figure of "0.064/l" should correctly read "0.128/l".

The error and its amendment appear to be obvious for the following reasons :

- 1) Generally, a molecular weight of polyurethane ( $\bar{M}_{pu}$ ) is calculated from the equation (1) as follows;

$$\bar{M}_{pu} = \frac{(1 - \alpha) \times 60.1 + 73.14 \times 2 \times \alpha + \bar{M}_{pp}}{\alpha} \dots (1)$$

wherein  $\alpha$  is a chemical equivalent ratio of diethylamine (hereinafter abbreviated as "DEA") to the total amines employed, and is represented by the following equation (2) since ethylenediamine ("EA") is bifunctional

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( $m_{EA}$ : a molar amount of EA,  $m_{DEA}$ : a molar amount of DEA), and

$\bar{M}_{pp}$  is a molecular weight of a prepolymer represented by the following equation (3)

$$\bar{M}_{pp} = \frac{N \times 250.3 + \bar{M}_{PG}}{N - 1} \dots \dots \dots \quad (3)$$

further wherein N is a molar ratio of 4,4'-diphenylmethane diisocyanate to polyetherglycol and is equal to 1.55 in Application Example of the present application, and  $\bar{M}_{PG}$  is a molecular weight of polyetherglycol and is equal to about 2000 in the reaction of the present Example as shown in Table 7 of the Specification.

- 2) In the present Example, the polymerization was carried out by setting the values of parameters as described above as follows;

$$\alpha = \frac{m_{DEA}}{2 \cdot m_{EA} + m_{DEA}} = 0.06, \quad N = 1.55 \text{ and } \bar{M}_{PG} \approx 2000$$

The calculation of a molecular weight of polyurethane ( $\bar{M}_{pu}$ ) according to the equations (3) and (1) by using these values as above leads to  $\bar{M}_{pu} = 73000$ .

On the other hand, the molecular weight of about 70,000 was also attained to by our measurement of viscosity of the polyurethane obtained.

- 3) When Application example 1 is described in the Specification, a calculation of a molar ratio of diethylamine to ethylenediamine ( $m_{DEA}/m_{EA}$ ) from the  $\alpha$  value should have been carried out correctly according to the equation

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but actually was carried out erroneously according to  
the equation  $m_{\text{eq}} =$

$$\alpha = \frac{m_{DEA}}{m_{EA} + m_{DEA}}$$

and accordingly the erroneous value of  $m_{DEA}/m_{EA} = 0.064$   
was attained to and described in the Specification, the  
correct value of  $m_{DEA}/m_{EA} = 0.128$  not being described.

- 4) In this connection, if the value of  $\frac{m_{DEA}}{m_{EA}}$   
 $= 0.064$  being used,  $\alpha = \frac{m_{DEA}}{m_{EA} + m_{DEA}} = 0.031$  is arrived at.  
 Further, when the  $\alpha$  value being used,  $M_p$  of 14100 is  
 arrived at which value is twice as high as compared  
 with the actual molecular weight of the polyurethane  
 prepared by us.

5) As explained above in 1) through 4), the value  
 $\frac{m_{DEA}}{m_{EA}} = 0.064$  as described in the Specification  
 is apparently an error originated in calculation, and  
 is correctly  $\frac{m_{DEA}}{m_{EA}} = 0.128$ .

In case the amendment should not be carried out at the time being it is requested that it be considered after the publication of the search report.

Patentanwalt  
(U. Schübel-Kopf)

Encl.:  
amended page 45 of the  
description

5-fold weight of the prepolymer of dimethylacetamide solvent and allowing the free isocyanate groups to react with equal moles of amines [a mixture of ethylenediamine and diethylamine; a molar ratio of diethylamine/  
5 ethylenediamine being  $\frac{0.128}{0.064}$ ] at  $70^{\circ}\text{C}$  for 3 hours. The polyurethane obtained had a molecular weight of about 70,000. The polyurethane was formed into a film with a thickness of 0.125 mm and a width of 1 mm and its low temperature recovery (recovery at  $10^{\circ}\text{C}$  ten seconds  
10 after release from elongation after the film had been elongated to 100 % at  $10^{\circ}\text{C}$  for 16 hours) was measured. The results are shown in Table 7, which shows excellent low temperature recovery of the copolymerized poly-  
etherglycol as compared with the polyurethane film  
15 employing PTMG.

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FIG. I

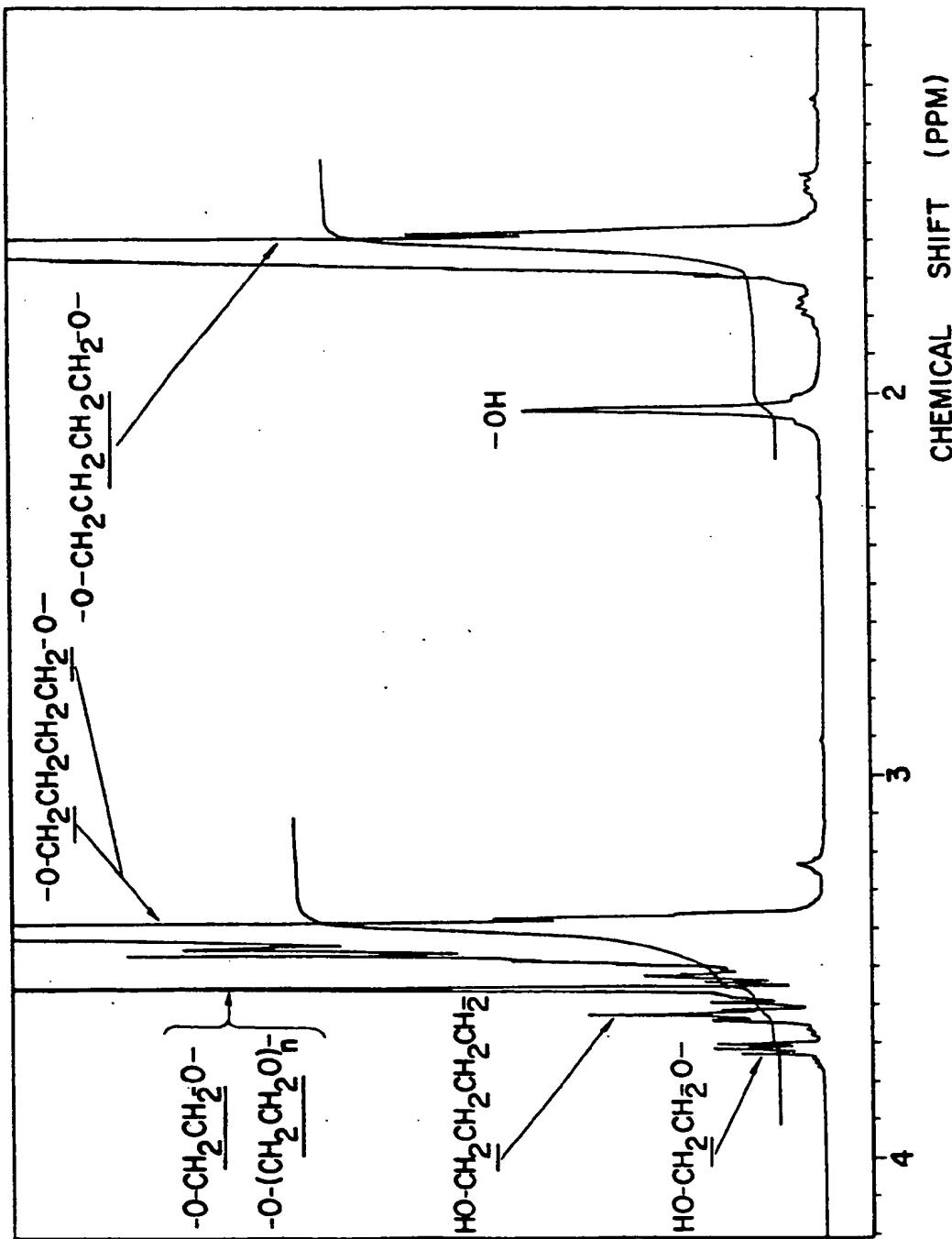
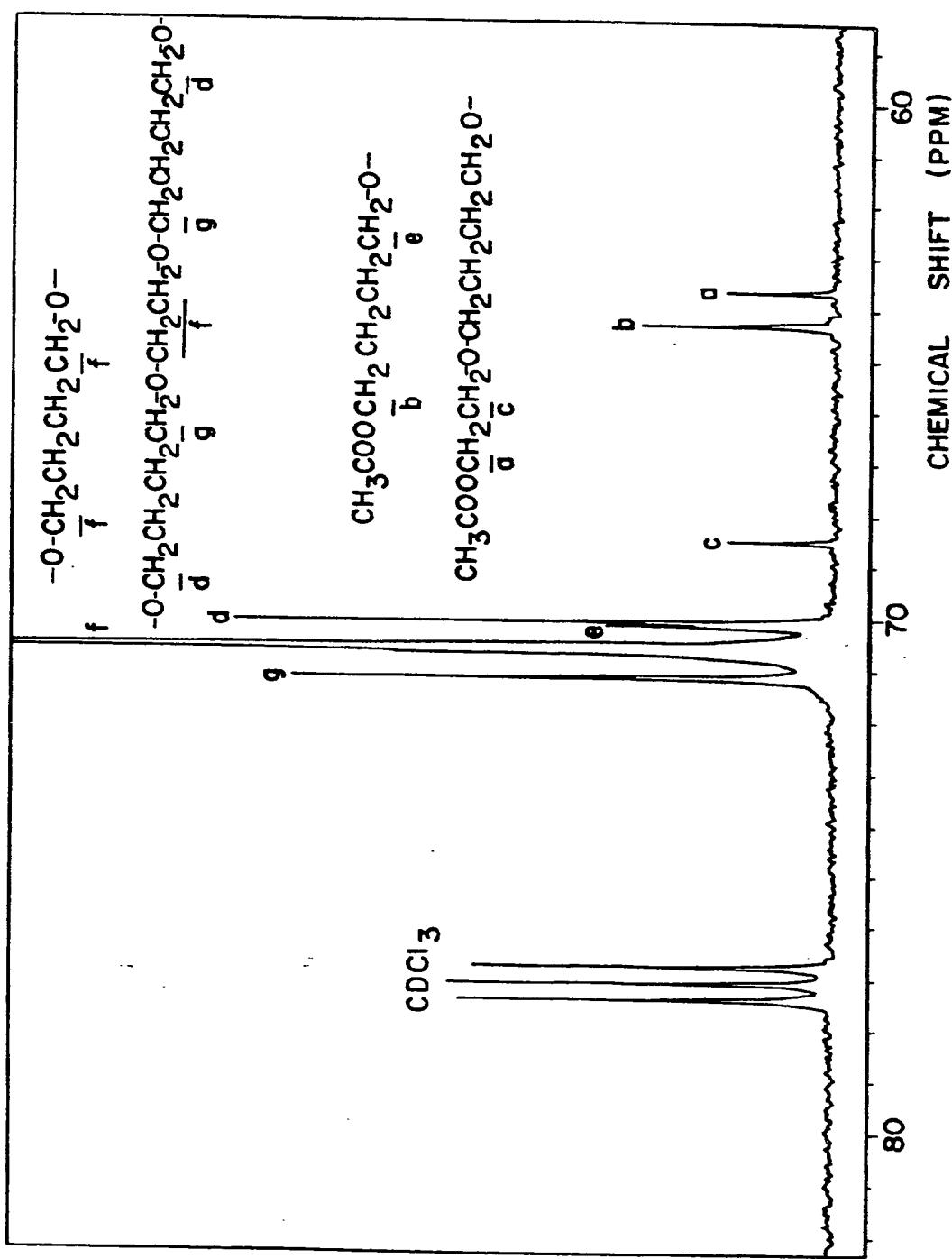


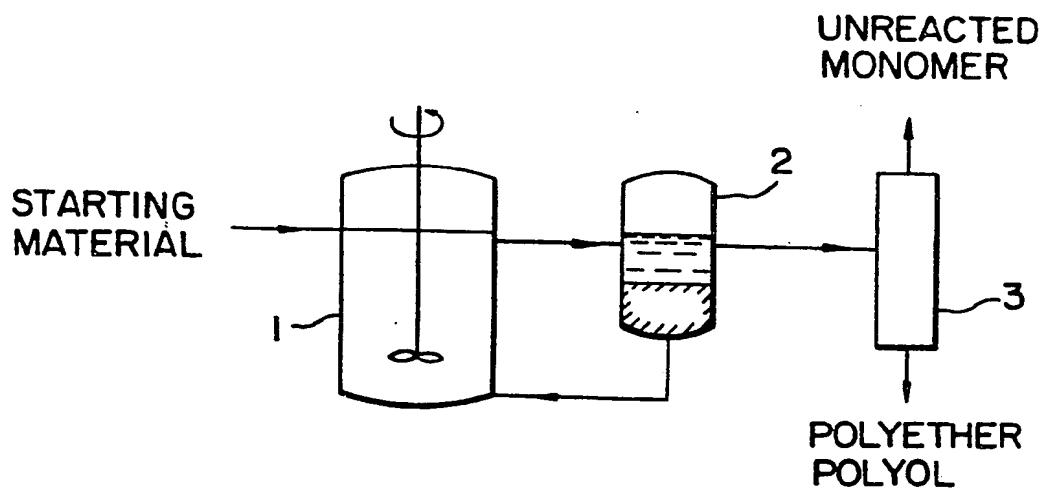
FIG. 2



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FIG. 3



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FIG. 4

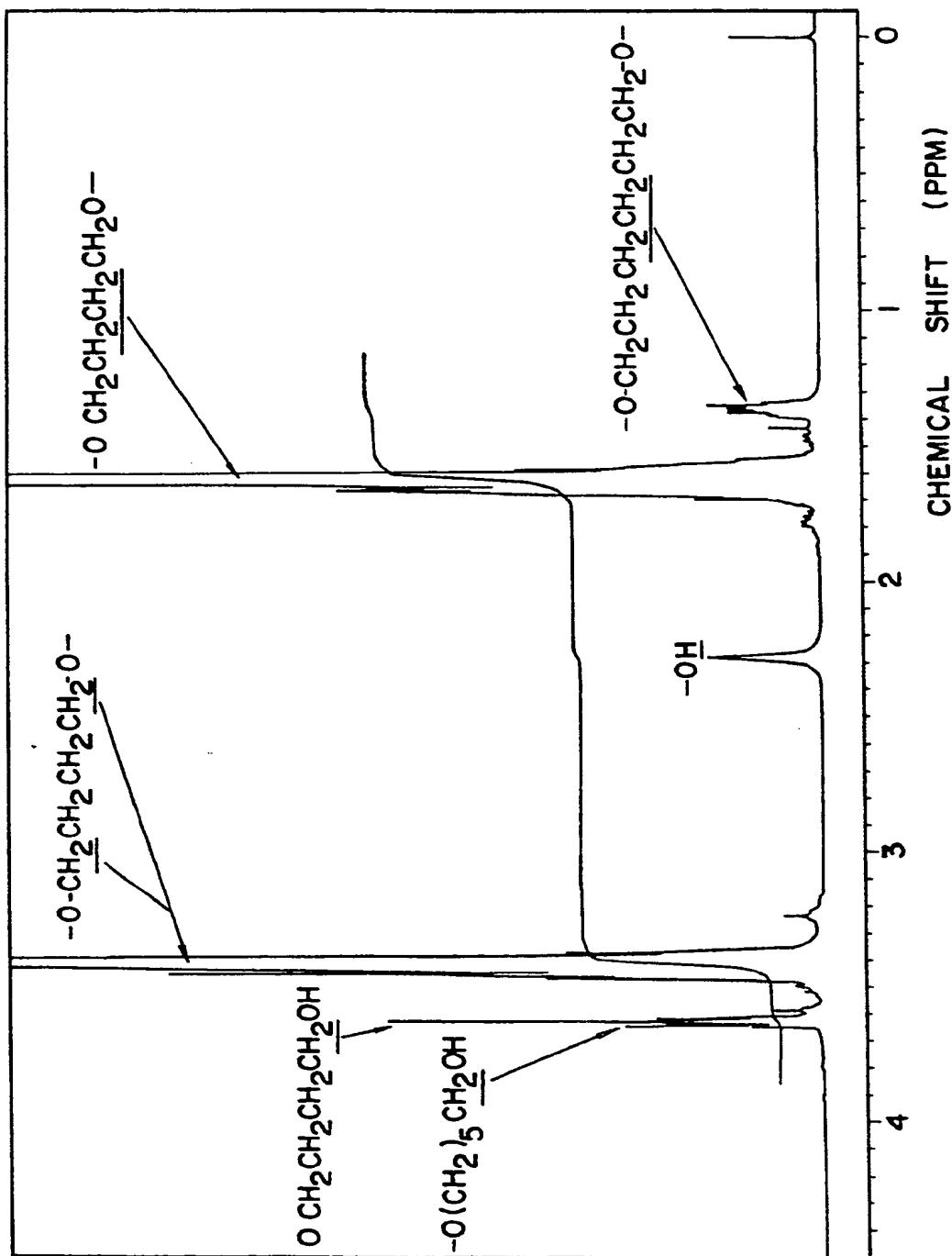
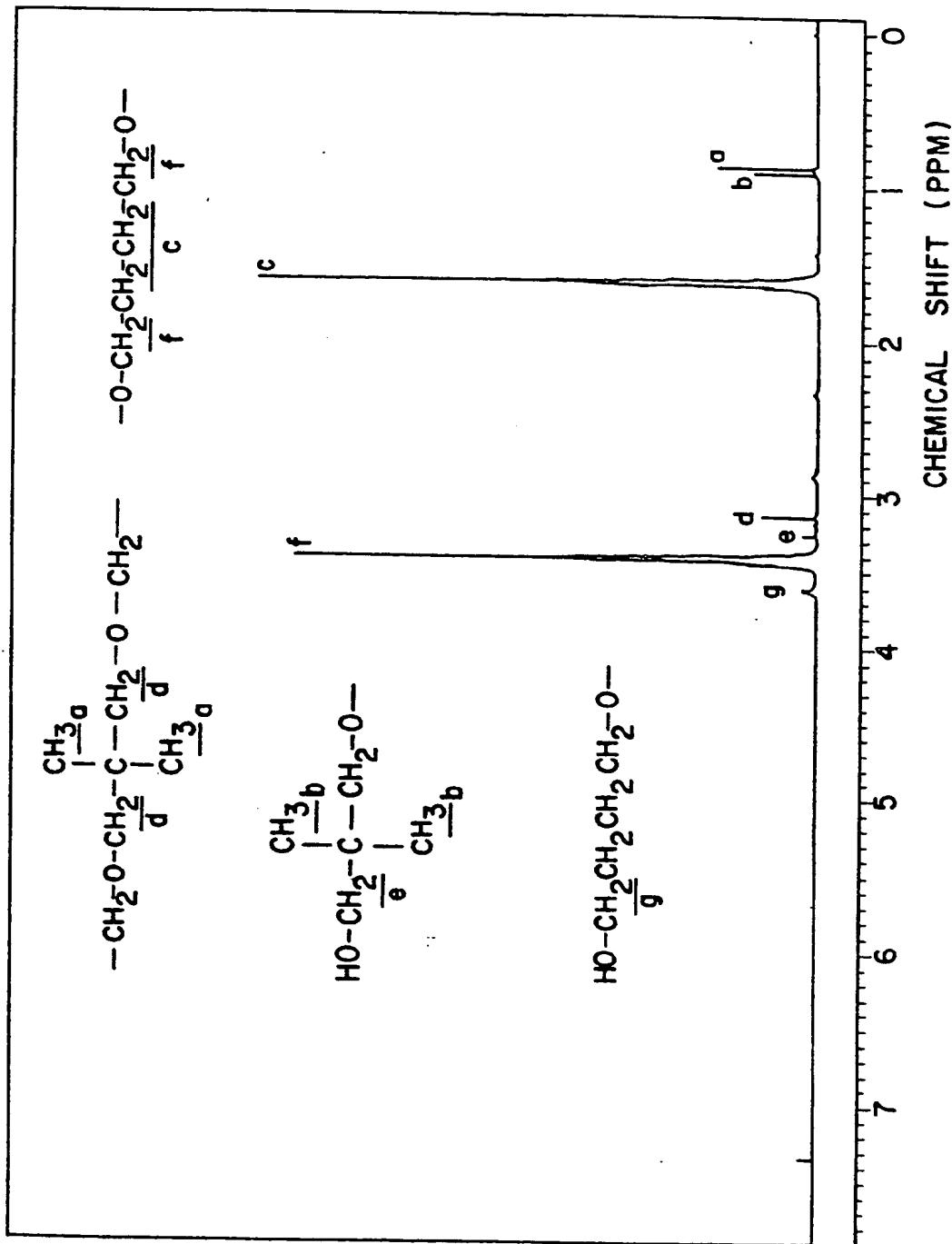
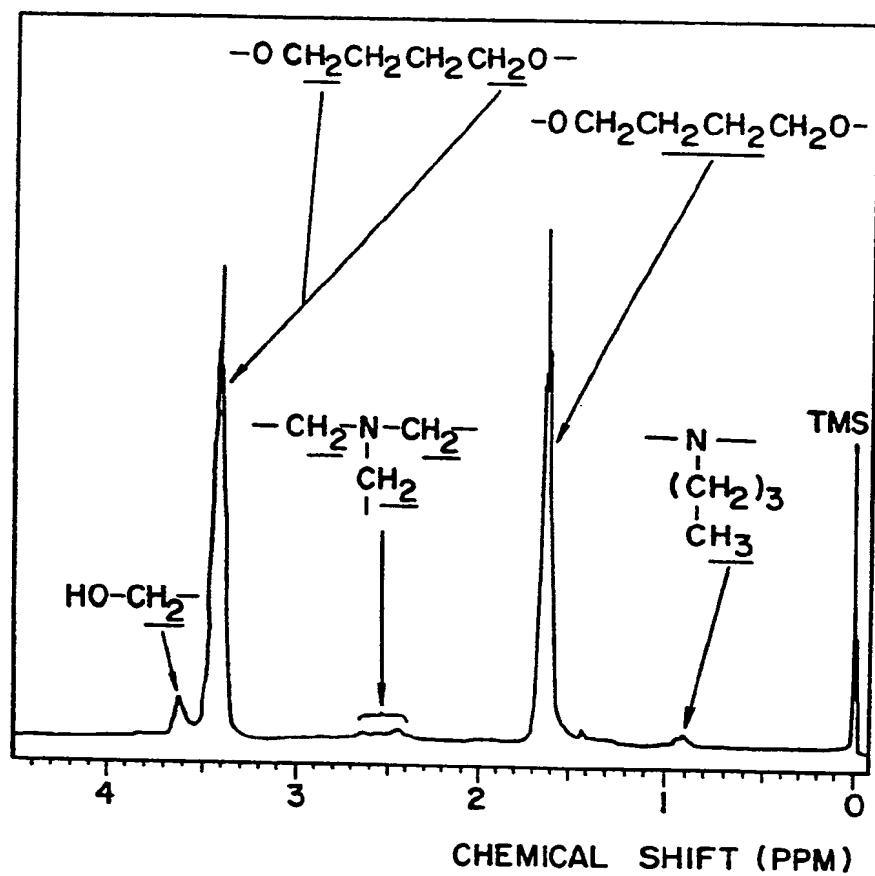


FIG. 5



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FIG. 6





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## EUROPEAN SEARCH REPORT

**0158229**

Application number

EP 85 10 3690

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P, A	EP-A-0 126 471 (ASAHI KASEI) * Claims 1-21 *	1-20	C 08 G 65/10 C 08 G 65/20 C 08 G 18/48
P, A	---	1	
A	PATENT ABSTRACTS OF JAPAN, vol. 9, no. 5, 10th January 1985, page (C-260) (1728); & JP-A-58-159824 (ASAHI GLASS) 10-09-1984		
A	---	1	
A	DE-B-1 520 750 (SUMITOMO) * Column 1, line 65 - column 2, line 65; claim *		
A	---	1	
A	PATENT ABSTRACTS OF JAPAN, vol. 7, no. 175, 3rd August 1983, page (C-179) (1320); & JP-A-58-83028 (DAICEL) 18-05-1983		
A	---	1	
A	US-A-3 454 652 (A.P. DUNLOP) * Whole document *		
	-----		
The present search report has been drawn up for all claims			
Place of search <b>BERLIN</b>	Date of completion of the search <b>21-06-1985</b>	Examiner <b>BOURGONJE A.F.</b>	
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